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(71) Applicants: CBL TECHNOLOGIES, INC. [US/US]; 3689
Brandy Rock Way, Redwood City, CA 94061 (US). MATSUSHITA ELECTRONICS CORPORATION [JP/JP]; 1-1,
Saiwai-cho, Takatsuki-shi, Osaka 569-1193 (JP).

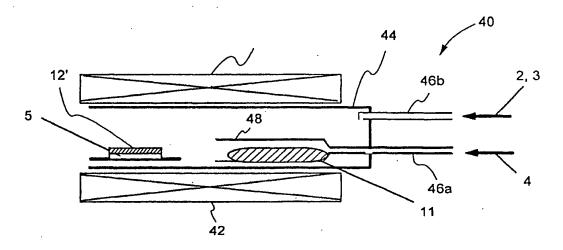
(72) Inventors: SOLOMON, Glenn, S.; 3689 Brandy Rock Way, Redwood City, CA 94061 (US). MILLER, David, J.; 1160 Village Drive, Belmont, CA 94002 (US). UEDA, Tetsuzo; 600 Sharon Park Drive #A201, Menlo Park, CA 94025 (US).

(74) Agent: ALBOSZTA, Marek; 426 Lowell Avenue, Palo Alto, CA 94301 (US). (81) Designated States: CN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

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(54) Title: MAGNESIUM-DOPED III-V NITRIDES & METHODS



(57) Abstract

Magnesium-doped high quality III-V nitride layers and methods for making the same. A p-type gallium nitride, indium nitride or aluminum nitride layer (12') may be produced on a sapphire substrate (5) by a hydride vapor-phase epitaxy (HVPE) process using a metal supply mixture which includes magnesium and a group III metal (Ga, In, Al) (11). The gallium nitride, indium nitride or aluminum nitride layer may be removed from the sapphire substrate to provide a Mg-dope III-V nitride substrate having low dislocation densities and being suitable for use in fabrication of, e.g. light-emitting devices.

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MAGNESIUM-DOPED III-V NITRIDES & METHODS

For

Tetsuzo Ueda, Glenn S. Solomon and David J. Miller

10 BACKGROUND OF THE INVENTION

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1. Field of the Invention

The present invention relates to magnesium-doped metal nitrides. The invention also relates to methods for growing magnesium-doped p-type III-V nitrides. The invention further relates to magnesium-doped group III metal nitride substrates grown by HVPE.

2. Background of the Related Art

Due to the nature of their band-gaps, III-V nitrides (nitrides of gallium, indium, and aluminum, and their alloys) show much promise in fabrication of light emitting devices for short wavelengths of the visible spectrum. For example, gallium nitride (GaN) is currently used in the manufacture of blue light emitting diodes, while nitride blue-violet lasers have been demonstrated as prototypes. By the term "III nitrides" is meant compounds consisting of one or more group III metals (including aluminum, gallium, and indium) as an electropositive

5 atom ligated by nitrogen atoms as some or all of the electronegative ligands (other electronegative ligands include phosphorus, arsenic or antimony). A typical formula for a group III metal nitride is $Ga_{1-x-y}Al_xIn_yN_{1-a-b-c}P_aAs_bSb_c$ [$0\le (x,x,a,b,c)\le 1$].

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However, the growth of low resistive p-type GaN (p-GaN) has proven to be problematic, using prior art methods and materials. Even magnesium having the shallowest acceptor level doped into GaN has resulted in highly resistive material. During the past decade, post annealing and electron beam 15 irradiation techniques have enabled the production of magnesium doped p-GaN of relatively low resistivity, by desorbing hydrogen atoms from the doped magnesium. However, the carrier concentration level is still around 1018 cm-3, and ohmic contact 20 resistance is not low enough to even match the level of conventional III-V semiconductor (e.g. GaAs) devices. high ohmic contact resistance results in high series resistance of a pn junction-based light emitting diode or laser diode. Thus, low voltage operation of these devices has been very difficult. Particularly in the case of laser diodes, this 25 leads to higher operating current and shorter lifetime of operation.

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According to prior art methods, p-type GaN has typically been grown by metal organic chemical vapor deposition (MOCVD) on sapphire substrates, in which bis-cyclopentadienylmagnesium (Cp₂Mg) acts as a source of magnesium dopant. Since the magnesium dopant in the resultant p-GaN is passivated with hydrogen atoms, post-annealing of the p-GaN in a nitrogen gas atmosphere is necessary to desorb the passivating hydrogen in order to achieve a carrier concentration of about 1018 cm-3. further drawback to prior art MOCVD techniques is that carbon atoms from the metal organic sources may be incorporated in the p-GaN film, resulting in carbon related deep level tending to decrease the p-type carrier concentration. In addition, prior art p-GaN layers grown by MOCVD have a high dislocation density (about 10° cm-2 on sapphire substrates). Furthermore, prior art MOCVD systems are complicated and expensive, due in part to the complex gas handling system, the high costs associated with metal-organics , and the use of a costly fixed temperature bath for the metal-organic source.

25 Another prior art technique used for growing p-GaN is hydride vapor phase epitaxy (HVPE). HVPE has certain advantages over MOCVD, in that lower dislocation densities (about 10⁷ cm⁻²) can

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be achieved using a relatively simple, low cost system by "bulk-like growth" with high growth rates. The lower dislocation density enables more reliable and higher performance devices to be fabricated, such as low threshold current laser diodes having a longer lifetime. Another advantage of HVPE is the absence of carbon in the source materials, with the result that higher activation efficiency of the dopants is expected, especially in the case of p-GaN.

The present invention provides an improved HVPE system for growing magnesium-doped p-type III-V nitrides, in a more cost-effective manner and with simpler equipment, as compared with prior art apparatus and methods.

5 SUMMARY OF THE INVENTION

According to one aspect of the invention, there is provided a simple and cost-effective method for growing Mg-doped p-type III-V nitride layers or substrates. A first reagent gas component may be provided by passing HCl source gas over a 10 mixture of a group III metal (gallium, Ga; indium, In; or aluminum, Al) and magnesium (Mg). A metallic mixture of this type is referred to as a group III/Mg metal mixture. resultant reagent gas (e.g., GaCl) reacts with ammonia in a HVPE system to form a p-type III-V nitride layer, the latter deposited on a suitable substrate. Using this method, p-GaN layers can be formed which have lower dislocation densities and less incorporated carbon atoms, as compared with layers formed using prior art methods. Lower dislocation densities are expected to lead to higher activation efficiency of the magnesium dopant. Furthermore, using the technique of the 20 invention, p-GaN substrates can be obtained by removing the p-GaN layer after HVPE growth.

Although hydrogen or nitrogen may be used as carrier gas in the practice of the invention, according to a currently preferred embodiment, nitrogen is used as carrier gas. The rationale for avoiding hydrogen as carrier gas is that hydrogen atoms from

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the hydrogen carrier gas may passivate magnesium in the grown III-V nitride film, thereby resulting in a lower p-type carrier concentration of the nitride layer. Minimizing the amount of hydrogen gas in the HVPE reactor enables higher p-type carrier concentration of the III-V nitride layer. This is advantageous for III-V nitrides used in light emitting devices.

According to a preferred embodiment of the invention, the temperature of the group III/Mg metal mixture is greater than 661 °C.

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One feature of the invention is that it provides a method for forming a Mg-doped p-type group III metal nitride layer by hydride vapor-phase epitaxy. Another feature of the invention is that it provides a Mg-doped p-type group III metal nitride layer, in which the Mg dopant is derived by passing HCl over elemental Mg.

One advantage of the invention is that it provides a simple and cost-effective method for forming a Mg-doped p-type group III metal nitride layer. Another advantage of the invention is that it provides a method for forming a p-type nitride layer in which hydrogen atom passivation of the magnesium dopant is

5 avoided.

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These and other objects, advantages and features are accomplished by the provision of a method of making a p-type nitride layer, including the steps of: a) providing a HVPE system including a reactor; b) arranging a substrate in the reactor; c) passing HCl over a metal mixture to provide a first reagent gas component, the metal mixture including magnesium metal; d)introducing ammonia and the first reagent gas component into the reactor; and e) growing a magnesium-doped p-type nitride layer on the substrate.

These and other objects, advantages and features are accomplished by the provision of a p-type nitride layer grown on a substrate by HVPE, the p-type nitride layer including: a group III nitride doped with magnesium, the p-type nitride layer formed by reacting a first reagent gas component with ammonia, the first reagent gas component prepared by passing HCl over a group III metal and magnesium metal.

25 These and other objects, advantages and features of the invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the

5 art upon examination of the following, or may be learned from practice of the invention. The advantages of the invention may be realized and attained as particularly pointed out in the appended claims.

5 BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 schematically represents an MOCVD growth system of the prior art;
- Fig. 2 schematically represents a HVPE growth system of the prior art;
- 10 Fig. 3A schematically represents a HVPE system suitable for growing Mg-doped p-type nitride layers, according to one embodiment of the invention;
 - Fig. 3B schematically represents a HVPE system suitable for growing Mg-doped p-type nitride layers, according to another embodiment of the invention; and
 - Fig. 4 schematically represents a series of steps involved in a method of making a p-type metal nitride layer, according to another embodiment of the invention.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

For purposes of illustration, the invention will be described with particular emphasis on the HVPE growth of p-type GaN. However, the invention is also applicable to the deposition of other III-V nitrides by HVPE.

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Referring now to the drawings, FIG. 1 schematically represents an MOCVD epitaxial growth system 20 of the prior art. System 20 includes furnace coils 22 situated around a reactor or growth tube 24, and a reactor inlet 26. A substrate 5, e.g., 15 sapphire, is arranged within reactor 24. Reagent and carrier gases are supplied to reactor 24 via a complex arrangement of tubing, as follows. Gallium is supplied from a gallium containing organo-metallic compound 7, such as trimethylgallium (TMGa), present in a first bubbler 28a, using a carrier gas 20 such as hydrogen 3. Ammonia 2 is supplied as a reagent gas via a lower sub-inlet 26b. Hydrogen 3 is also used as a carrier gas for a magnesium containing compound 8, such as biscyclopentadienylmagnesium (Cp2Mg), contained in a second bubbler 28b. Compound 8 provides the Mg required for magnesium 25 doping. It is also noted that hydrogen 3 is also supplied to reactor 24 via an upper sub-inlet 26a. Mass flow meters are used to control the gas flow rates. As a result of supplying

5 TMGa 7, ammonia 2, and Cp₂Mg 8 to reactor 24, p-GaN 12 is grown as a wafer on substrate 5. Subsequently, the wafer is annealed in a nitrogen atmosphere to desorb the hydrogen atoms from the doped magnesium. The resultant hole concentration in the p-GaN layer (12) is up to 10¹⁸ cm⁻³.

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Another prior art method for forming p-type III-V nitride layers is Mg-doping using a HVPE system. Fig. 2 schematically represents a HVPE growth system 30 of the prior art. Briefly, system 30 includes a first furnace 32a surrounding a reactor or growth tube 34. Reactor 34 has first and second reactor inlets, 36a, 36b, respectively, and a production chamber 35. Production chamber 35 houses a supply of liquid group III metal 9 (Ga, In, or Al, or alloys thereof). Reagent gas (ammonia 2) and carrier gas (hydrogen 3) are supplied to reactor 34 via second inlet 36b. HCl (precursor or source gas) 4 is supplied via first inlet 36a to chamber 35, where HCl 4 reacts with metal 9 to form reagent gas, such as GaCl.

In system 30, a source of magnesium dopant is in the form of 25 magnesium metal 10 housed within a dopant chamber 38. Dopant chamber 38 and magnesium 10 are heated by a second furnace 32b.

System 30 uses a separate furnace for magnesium 10; therefore

the temperature of dopant chamber 38, on the one hand, and the temperature of reactor 34 and production chamber 35, on the other hand, can be controlled independently. However, as a result of this arrangement, system 30 becomes more complicated as well as more costly.

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In view of the above, it can be readily appreciated that an improved system and method for HVPE growth of P-type III-V nitride layers is required. Fig. 3A schematically represents a HVPE system 40 suitable for growing Mg-doped p-type nitride layers, according to one embodiment of the invention. System 40 includes a furnace 42 surrounding a reactor 44 having first and second inlets 46a, 46b, respectively. First inlet 46a leads to production chamber 48. A substrate 5, such as sapphire, is arranged within reactor 44.

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Production chamber 48 houses a supply of a group III metal (Ga, In, or Al) together with elemental (metallic) magnesium, but may also be a chloride of magnesium. Preferably, the group III metal and the magnesium source are combined to form a group III/Mg metal mixture 11. The magnesium component of mixture 11 serves as the source of the Mg dopant in system 40. Preferably the magnesium is a relatively minor component of mixture 11;

more preferably the magnesium component of mixture 11 is in the range of 10 ppm to 10,000 ppm. Mixture 11 is heated by furnace 42 to a temperature in the range of from 500 to 1000 °C; more preferably in the range of from 600 to 900 °C; and most preferably to a temperature of from 650 to 750 °C.

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HCl 4 is introduced into chamber 48 via first inlet 46a, where the HCl reacts with mixture 11 to provide a first reagent gas component which is carried into reactor 44. Preferably, the first reagent gas component is composed primarily of a chloride of Ga, In, or Al, such as GaCl, with lesser amounts of Mg. According to the embodiment represented in Fig. 3A, a second reagent gas component, ammonia 2, is supplied to reactor 44 via second inlet 46b using hydrogen as carrier gas. The first and second reagent gas components react in reactor 44 to form a p-type nitride layer 12', e.g., of GaN, which is deposited on substrate 5.

After the growth of layer 12' as a relatively thick film, e.g., as a film of p-GaN, layer 12' may be removed from sapphire substrate 5 to provide a p-GaN substrate. Layer 12' may be grown to a thickness in the range of from 5.0 micron to 500 micron; more preferably to a thickness of 100 micron.

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According to the invention, system 40 may be used for the cost-effective production of Mg-doped p-type group III nitride (e.g., p-GaN) layers. Such layers are formed in the absence of organic compounds, so that there is no carbon incorporated into the nitride layer. Carbon related deep level traps reduce the carrier concentration. Thus, the absence of carbon represents a significant advantage over prior art MOCVD techniques, in that it allows for higher carrier concentration.

15 Fig. 3B schematically represents a HVPE system 40' suitable for growing Mg-doped p-type III-V nitride layers, according to another embodiment of the invention. System 40' is substantially similar to system 40, described hereinabove with reference to Fig. 3A. However, in system 40' nitrogen gas 6 is 20 used as a carrier gas for ammonia 2 at inlet 46b, instead of hydrogen 3 (Fig. 3A). By using nitrogen 6 as a carrier gas to the exclusion of hydrogen 3, passivation of magnesium atoms in p-GaN film 12'' by hydrogen atoms is greatly decreased. Thus, in the absence of hydrogen 3 carrier gas, passivation is 25 limited to that caused by relatively trace quantities of hydrogen produced during decomposition of ammonia and HCl. The resultant p-type film 12'' shows lower resistivity than films

5 12, 12' grown according to systems and methods which use hydrogen as carrier gas (Figs. 1, 2, 3A).

Fig. 4 schematically represents a series of steps involved in a method of making a Mg-doped p-type metal nitride layer, according to another embodiment of the invention, in which step 50 involves providing a HVPE system. A HVPE system provided in step 50 may be, for example, either of the systems 40, 40' described hereinabove with reference to Figs. 3A and 3B, respectively. Step 52 involves arranging a substrate in the 15 reactor of the HVPE system. The substrate arranged in the reactor in step 52 is preferably a sapphire substrate.

Step 54 involves passing a source gas including HCl over liquid metal. The liquid metal over which the HCl is passed in step 54 includes magnesium or a magnesium source (such as a magnesium chloride), and a group III metal selected from the group consisting of Ga, In, Al, and alloys of Ga, In, and Al. According to a currently preferred embodiment, elemental (metal) magnesium and the group III metal are combined to form 25 a group III/Mg metal mixture, and the HCl is passed over the group III/Mg metal mixture. Typically, the magnesium is present in the group III/Mg metal mixture in relatively trace

5 amounts, e.g., 100 pmm, but may be in any range between 1 ppb (parts-per-billion) and to 10,000 ppm (parts per million).

Preferably, the group III/Mg metal mixture is heated to a temperature in the range of 650 °C to 900 °C. Step 54 results in the formation of a first reagent gas. This first reagent gas component includes magnesium and a chloride of a group III metal, e.g., GaCl or InCl.

Step 56 involves introducing reagent gases into the HVPE reactor. Reagent gases introduced into the reactor include the first reagent gas component formed as a result of step 54, and a second reagent gas component. Preferably, the second reagent gas component is ammonia. The second reagent gas component is introduced into the reactor by means of a carrier gas. The carrier gas for introduction of ammonia is preferably nitrogen, although other gases such as hydrogen may also be used. As mentioned hereinabove, nitrogen is preferred over hydrogen as carrier gas, since hydrogen gas leads to passivation of Mg dopant in the nitride layer.

25 Step 58 involves growing the group III nitride layer on the substrate. The group III nitride layer grown in step 58 results from the vapor phase reaction between ammonia gas and

the first reagent gas component. As an example, the group III nitride layer may be a Mg-doped GaN layer formed by reaction of ammonia with GaCl in the presence of minor quantities of magnesium. Step 58 may involve growing the group III nitride layer to a thickness of up to 300 micron or more. The desired thickness of the group III nitride layer grown in step 58 will depend on factors such as the intended application of the layer. After the group III nitride layer has been grown to the desired thickness, it may be removed from the sapphire substrate in step 60. For example, by polishing the backside of the structure, the sapphire substrate may be removed.

The method of Fig. 4 provides a Mg-doped p-type group III nitride substrate having low dislocation density and high carrier concentration. The preceding steps described with 20 reference to Fig. 4 provide a relatively simple and costeffective method for forming Mg-doped p-type group III nitrides. No organic source materials are used in the method of Fig. 4. Therefore, as compared with similar materials formed by MOCVD, higher activation efficiency of the dopant is expected, especially in the case of p-GaN.

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5 It is preferable that the temperature of the group-III/Mg mixture 11 of systems 40 and 40° be maintained at a temperature above about 660.45 °C. The rationale for stipulating this temperature is as follows. The commonly used group-III metals for III-V nitride semiconductors are gallium, aluminum, and indium, having melting points of 29.8 °C, 660.45 °C, 156.6 °C, respectively. Since the melting point of magnesium is 650 °C, the common group-III/Mg mixture 11 is in the liquid phase at a temperature above 660.45 °C. At this temperature (660.45 °C), sufficient magnesium can be incorporated in film 12'/12' to achieve low resistive p-type III-V nitrides, because no undesirable alloys (such as Mg₃Ga₂) is present in the group-III/Mg metal supply.

The foregoing embodiments are merely exemplary and are not to be construed as limiting the present invention. The present teaching may be applied to other types of apparatuses and methods. The description of the present invention is intended to be illustrative, and not to limit the scope of the appended claims. Many alternatives, modifications, and variations will be apparent to those skilled in the art.

5 WHAT IS CLAIMED IS:

- 1. A method of making a p-type nitride layer, comprising the steps of:
 - a) providing a HVPE system including a reactor;
 - b) arranging a substrate in the reactor; and
- c) introducing reagent gases into the reactor, wherein the reagent gases include a first reagent gas component, the first reagent gas component prepared by passing HCl over a group III metal and Mg.
- 15 2. The method of claim 1, wherein the group III metal comprises Ga, In, Al, or one of their alloys.
- 3. The method of claim 1, wherein the group III metal and the Mg are combined to form a group III/Mg metal mixture prior to passing HCl over the group III metal and the Mg.
 - 4. The method of claim 3, wherein the Mg of the group III/Mg metal mixture is elemental Mg.
- 25 5. The method of claim 3, wherein the group III/Mg metal mixture consists essentially of at least one group III metal and elemental magnesium.

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- 6. The method of claim 3, wherein the group III/Mg metal mixture comprises from 1 parts-per-billion to 10,000 parts-per-million of Mg metal.
- The method of claim 1, wherein the reagent gases further include ammonia, and the ammonia is carried to the reactor via a carrier gas.
- 8. The method of claim 7, wherein the carrier gas is free from hydrogen.
 - 9. The method of claim 7, wherein the carrier gas is a gas selected from the group consisting of nitrogen and helium.
- 20 10. The method of claim 1, wherein the first reagent gas component comprises a chloride of a group III metal and magnesium.
- 11. The method of claim 10, wherein the first reagent gas
 25 component further comprises a chloride of magnesium.

5 12. The method of claim 3, wherein the group III/Mg metal mixture is heated to a temperature of 660 °C to 900 °C.

13. The method of claim 3, wherein the HVPE system further includes a production chamber, the group III/Mg metal mixture is housed within the production chamber, and the HCl is passed into the production chamber and over the group III/Mg metal mixture.

- 14. The method of claim 1, wherein the p-type nitride layer is doped with magnesium, and the magnesium component of the p-type nitride layer is minimally passivated with hydrogen atoms.
- 15. The method of claim 1, wherein said step c) comprises

 20 introducing ammonia and the first reagent gas component

 into the reactor, wherein the ammonia and the first reagent

 gas component react to form a Mg-doped p-type group III

 metal nitride on the substrate.
- 25 16. The method of claim 1, wherein the p-type nitride layer has a dislocation density is less than $10^7/\mathrm{cm}^2$ to and a resistivity value less than 0.1 ohms cm.

- 17. The method of claim 1, wherein the p-type nitride layer is formed on the substrate to a thickness of from 50 micron to 500 micron
- 10 18. The method of claim 1, wherein the p-type nitride layer comprises Mg-doped p-GaN.
 - 19. The method of claim 1, further comprising the step of:
- d) after said step c), removing the p-type nitride layer

 from the substrate arranged in said step b).
- 20. A p-type nitride layer grown on a substrate by HVPE, said p-type nitride layer comprising: a group III nitride doped with magnesium, the p-type nitride layer formed by reacting a first reagent gas component with ammonia, the first reagent gas component prepared by passing HCl over a group III metal and magnesium metal.
- 21. The p-type nitride layer of claim 20, wherein the group

 25 III metal comprises Ga, In, Al, or one of their alloys.

5 22. The p-type nitride layer of claim 20, wherein the group III metal and the Mg comprise a group III/Mg metal mixture.

- 23. The p-type nitride layer of claim 22, wherein the group

 10 III/Mg metal mixture comprises from 1 parts-per-billion to

 10,000 parts-per-million of Mg metal.
- 24. The p-type nitride layer of claim 20, wherein the group III/Mg metal mixture comprises from 1 parts-per-billion to 10,000 parts-per-million of Mg metal.
 - 25. The p-type nitride layer of claim 20, wherein the group III/Mg metal mixture consists essentially of at least one group III metal and elemental magnesium.

- 26. The p-type nitride layer of claim 20, wherein the first reagent gas component comprises a chloride of a group III metal, and Mg.
- 25 27. The p-type nitride layer of claim 26, wherein the first reagent gas further comprises a chloride of Mg.

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- 5 28. The p-type nitride layer of claim 22, wherein the group III/Mg metal mixture is heated to a temperature of 660 °C to 900 °C.
- 29. The p-type nitride layer of claim 20, wherein the magnesium component of the p-type nitride layer is minimally passivated with hydrogen atoms.
 - 30. The p-type nitride layer of claim 20, wherein the p-type nitride layer has a dislocation density is less than $10^7/\mathrm{cm}^2$ to and a resistivity value less than 0.1 ohms cm.
 - 31. The p-type nitride layer of claim 20, wherein the p-type nitride layer is formed on the substrate to a thickness in the range of 50 micron to 500 micron.

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- 32. The p-type nitride layer of claim 20, wherein the p-type nitride layer comprises Mg-doped p-GaN.
- 33. A method of making a p-type nitride layer, comprising the steps of:
 - a) providing a HVPE system including a reactor;
 - b) arranging a substrate in the reactor;

c) passing HCl over a metal mixture to provide a first reagent gas component, the metal mixture including magnesium metal;

- d) introducing ammonia and the first reagent gas component into the reactor; and
- e) growing a magnesium-doped p-type nitride layer on the substrate.
 - 34. The method of claim 33, wherein the metal mixture comprises elemental magnesium and a group III metal, the group III metal selected from the group consisting of Ga, In, and Al.
 - 35. The method of claim 33, wherein the group III/Mg metal mixture comprises from 1 parts-per-billion to 10,000 parts-per-million of Mg metal.

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- 36. The method of claim 33, further comprising the step of:
 - f) after said step e), removing the p-type nitride layer from the substrate.

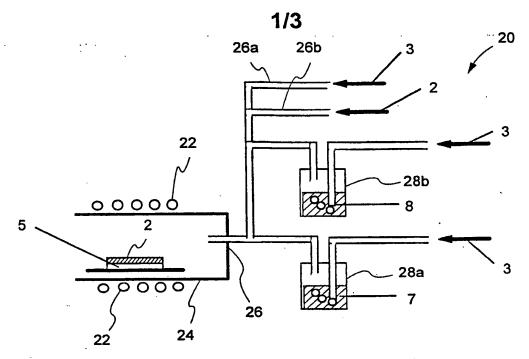


FIG. 1

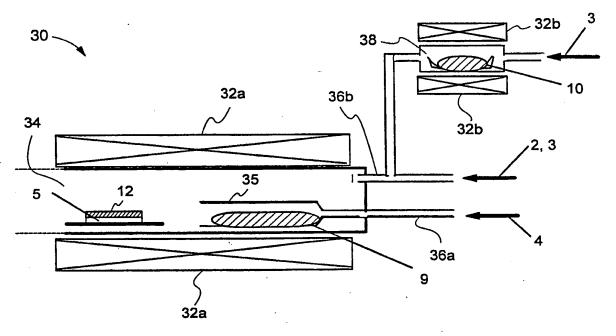


FIG. 2

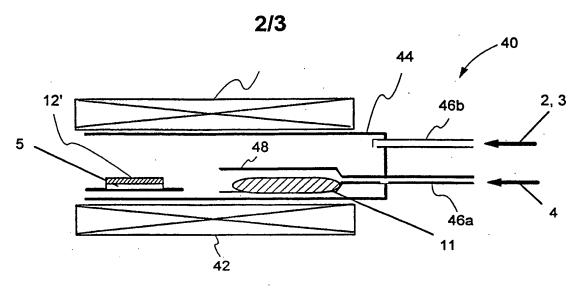


Fig. 3A

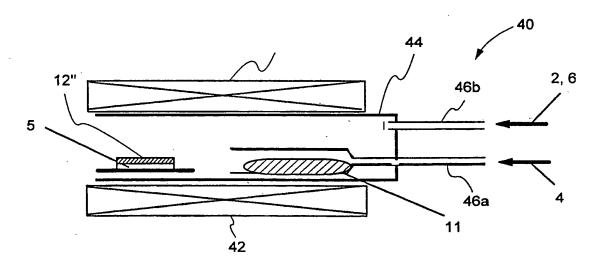


Fig. 3B

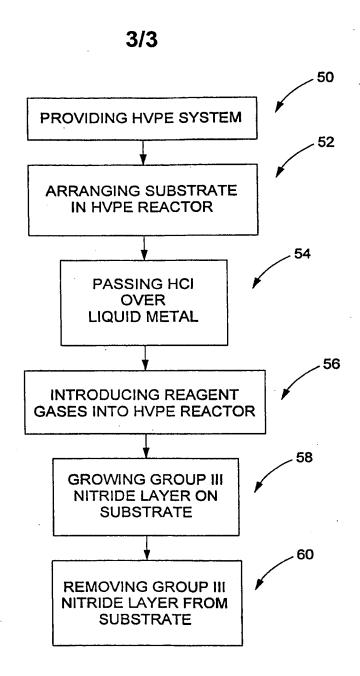


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER								
IPC(7) : C30B 23/02, 25/14, 25/18,29/38, 29/40								
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Categ	ory *	Citation of document, with indication, where ap	propriate,	of the relevant passages	Relevant to claim No.			
Y		JP 08-335,555 A (SATO et al) 17 December 1996 (1		igure i	1-36			
Α	- 1	US 3,901,746 A (BOUCHER) 26 August 1975 (26.0		- 1				
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	Further	documents are listed in the continuation of Box C.		See patent family annex.				
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/10150

Continuation of B. FIELDS SEARCHED Item 3: WEST 2.0, CAS ONLINE search terms: nitirde, mg, sapphire substrate

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